DECLARATION

I, Takeshi WATANABE, c/o Watanabe & Associates, Kanda-Nishikicho Bldg., 6F, 1-6 Kanda-Nishiki-cho 1-chome, Chiyoda-ku Tokyo, Japan, do solemnly and sincerely declare that I am well acquainted with both the Japanese language and the English language and that the attached English translations of Japanese Patent Application Nos. 2001-068883 and 2001-079680 are true and correct translation to the best of my knowledge and belief from the Japanese language to the English language.

Dated this 29th day of October 2003

Takeshi Watanabe

Takeshi Watanabe

(Translator)

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[Indication of Charge]

[Number of Advanced payment Ledger] 013169

[Amount of Payment] ¥21000

[List of submitting Material]

[Material] Specification 1

[Material] Abstract 1

[Proof] Require

[DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] TONER FOR MICR

[CLAIMS FOR PATENT]

[Claim 1] A toner for MICR which comprises a binder resin, magnetite particles and a wax, said magnetite particles comprising granular magnetite and acicular magnetite, wherein a ratio by weight of said acicular magnetite in said magnetite particles is 0.1 - 0.5 to the granular magnetite of 1.0, said magnetite particles are included in an amount of 15 - 50 % by weight in the toner, and said wax has a melting point measured by DSC of 60 - 100°C.

[Claim 2] A toner for MICR according to Claim 1, wherein said granular magnetite has residual magnetization of 5 - 15 emu/g and saturation magnetization of 70 -95 emu/g, and said acicular magnetite has residual magnetization of 20 - 50 emu/g and saturation magnetization of 70 -95 emu/g.

[Claim 3] A toner for MICR according to Claim 1 wherein said Fischer-Tropsch wax is natural gas type Fischer-Tropsch wax.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[TECHNICAL FIELD OF THE INVENTION]

The present invention relates to a toner for MICR (magnetic ink character recognition) capable of printing magnetic images by a printer of one-component magnetic developing system.

[0002]

[PRIOR ART]

In recent years, documents capable of magnetic ink character recognition (MICR) and particularly checks or bills have been easily prepared by one-component magnetic developing system with a magnetic toner. The MICR that is a system of reading magnetized images by a magnetic head is not conveniently

used because images are obtained by offset printing with magnetic ink. A process of printing with a two-component developer which has been put to practical use is not also conveniently used, because the process requires a large-sized machine as compared with that for the one-component developer. As small-sized printers, there are those for heat-sensitive transfer processes. However, almost all of them are single-purpose machines for printing only MICR characters. It is accordingly desired to develop a small-sized printer capable of printing characters or symbols together with the MICR characters. Regarding the use for MICR, the one-component developing process has been developed hitherto because of using a compact machine, keeping easy maintenance and being capable of printing images other than MICR characters.

[0003]

In the prior art, magnetic materials having large magnetization were attempted to use for the toner for MICR. Japanese Laid-open Patent Publication Nos. Hei 6-282100 and Hei 7-271085 discloses the use of acicular magnetite. The acicular magnetite has, however, problems that it is easily exposed on the surface of toner particles and is easily released from the toner particles by sliding friction with a magnetic head. Although appropriate saturation magnetization is necessary for development by the one-component magnetic developing process, signal strength becomes too high when the acicular magnetite is added in an amount necessary to development. The amount of the acicular magnetite is restricted because of its inferior dispersing ability. It is therefore difficult to satisfy both of the saturation magnetization required for development and the residual magnetization required for signal strength. It is furthermore impossible to satisfy every requirement even if it is used together with magnetite of other

type.

[0004]

The Japanese Laid-open Patent Publication Nos. Hei 6-282100, 6-43689 and 7-271085 discloses addition of various kinds of waxes to a toner for MICR in order to improve resistance against sliding friction. The resultant toner however often causes problems in magnetic reading even if the image formed has no problem in reading by eyes.

[0005]

In the prior arts, as above-mentioned, there is no MICR toner which satisfies excellent resistance against sliding friction with the magnetic head and appropriate signal strength and forms magnetic images having stabilized image density and good image quality upon copying a number of sheets, without hurting image density and image quality such as, fog, lacking or omission of characters, fine line reproducibility, etc.

[0006]

[PROBLEM TO BE SOLVED BY THE INVENTION]

An object of the present invention is to provide a toner for MICR having sufficient resistance against sliding friction with the magnetic head, having appropriate signal strength by which reading errors are not caused, and having no trouble in image qualities such as image density, fog, etc.

[0007]

[MEANS FOR SOLVING THE PROBLEMS]

A toner for MICR of the present invention comprises a binder resin, magnetite particles, and a wax, as essential components. It is also preferred that the toner contains a charge controlling argent which preferably consists of at least two charge controlling materials, at least one of which is a chrome azo dye.A toner for MICR of the present invention comprises a binder resin, magnetite particles and a wax, said

magnetite particles comprising granular magnetite and acicular magnetite, wherein a ratio by weight of said acicular magnetite in said magnetite particles is 0.1 - 0.5 to the granular magnetite of 1.0, said magnetite particles are included in an amount of 15 - 50 % by weight in the toner, and said wax has a melting point measured by DSC of 60 - 100°C.

It is preferred that said granular magnetite has residual magnetization of 5 - 15 emu/g and saturation magnetization of 70 - 95 emu/g, and said acicular magnetite has residual magnetization of 20 - 50 emu/g and saturation magnetization of 70 - 95 emu/g.

Furthermore, it is preferred that said Fischer-Tropsch wax is natural gas type Fischer-Tropsch wax.

[0008]

[EMBODIMENTS OF THE INVENTION]

The toner for MICR according to the present invention comprises at least a binder resin, a magnetic material and a wax, as main components, and contains, if necessary, a coloring agent, a releasing agent other than the wax, a charge controlling agent and other additives. A fluidizing agent may also be allowed to attach to the surface of toner particles.

Specific examples of the binder resin of the toner according to the present invention include homopolymers and copolymers of styrene and substituted styrene such as polystyrene, poly-p-chlorostyrene, polyvinyltoluene, styrene-p- chlorostyrene copolymer, styrene-vinyltoluene copolymer, etc.; copolymers of styrene and acrylic acid ester such as styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-n-butyl acrylate copolymer, etc.; copolymers of styrene and methacrylic acid ester such as styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-n-butyl methacrylate

copolymer, etc.; styrene-acrylic acid ester-methacrylic acid ester terpolymer; styrene copolymers composed of styrene and other vinyl monomers such as styrene-acrylonitrile copolymer, styrene-vinyl methyl ether copolymer, styrene-butadiene copolymer, styrene-vinyl methyl ketone copolymer, styrene-acrylonitrile-indene copolymer, styrene-maleic acid ester copolymer, etc.; polymethyl methacrylate, polybutyl methacrylate, polyacrylic acid ester resin, polyester resin, polyvinyl acetate, polyamide resin, epoxy resin, polyvinyl butyral resin, polyacrylic acid- phenol resin, phenol resin, aliphatic or alicyclic hydrocarbon resin, petroleum resin, chlorinated paraffin, polyvinyl chloride, polyvinylidene chloride, etc., which can be used alone or as a mixture of two or more of them.

Of these resins, styrene-acrylic acid ester copolymer resin and polyester resin are preferably used in the present invention.

[0009]

The magnetite particles incorporated in the toner for MICR of the present invention are composed at least of granular magnetite and acicular magnetite. In this toner, the ratio by weight of said acicular magnetite in said magnetite particles should be 0.5 or less to 1.0 of the granular magnetite. It is preferred in the present invention that the acicular magnetite is in a range of 0.10 -0.50, and more preferably 0.20 -0.45, to 1.0 of the granular magnetite. When the ratio by weight of the acicular magnetite to the granular magnetite is in excess of 0.50, the signal strength exceeds an appropriate range.

Furthermore, the content of the magnetite particles in the toner should be in a range of 15 - 50% by weight and preferably 20 - 45% by weight. When the amount of the magnetite particles is lower than 15% weight, saturation magnetization necessary

for the development and residual magnetization necessary for the development cannot be obtained. When the amount of it is in excess of 50% by weight, there are problems that fixing strength reduces to cause deterioration of the resistance against sliding friction, that the saturation magnetization is in excess of the value required for the development, and that the signal strength exceeds the appropriate level.

The granular magnetite used in the present invention include those having irregular, spherical, hexahedral and octahedral shapes.

The granular magnetite used in the present invention is preferred to have the residual magnetization in a range of 5 - 15 emu/g, and particularly 8 - 13 emu/g. The saturation magnetization of it is preferred to be in a range of 70 - 95 emu/g, and particularly 75 - 85 emu/g. Conventional granular magnetite having a particle size of 0.2 - 0.3 micrometers and an aspect ratio of less than 2.0 can be used in the present invention. The residual magnetization of higher than 15 emu/g brings about excess magnetization and excess signal strength, while the residual magnetization of lower than 5 emu/g causes lack of the signal strength to result in reading errors. When the saturation magnetization is lower than 70 emu/g, such saturation magnetization is insufficient for the development. On the other hand, when it exceeds 95 emu/g, it shows a tendency to exceeding the saturation magnetization necessary for the development.

The acicular magnetite used in the present invention is preferred to have the residual magnetization in a range of 20 - 50 emu/g, and particularly 25 - 40 emu/g. The saturation magnetization of it is preferred to be in a range of 70 - 95 emu/g, and particularly 75 - 85 emu/g. Conventional acicular magnetite having a particle size of approximately 0.6

micrometers and an aspect ratio of 2.0 or more can be used in the present invention. The residual magnetization of lower than 20 emu/g causes the lack of signal strength and that of higher than 50 emu/g brings about excess signal strength. The saturation magnetization of lower than 70 emu/g does not bring the saturation magnetization necessary for the development and that of higher than 95 emu/g shows a tendency to exceeding the saturation magnetization necessary for the development.

Other magnetic materials can be used, if necessary, together with the granular magnetite and the acicular magnetite.
[0010]

To the toner for MICR according to the present invention, the wax is added in order to ensure excellent releasing property between a heating roll for fixation and the toner or to ensure the excellent resistance against sliding friction with the magnetic head. In such a case, it is preferred to add the wax having a DSC melting point in a range of 60 - 110°C and particularly 85 - 100°C. The wax having the DSC melting point of lower than 60°C easily causes problems in preservation stability of the toner and also becomes to have poor fluidity. When the DSC melting point of it is higher than 110°C, the wax has inferior low temperature fixability because of a poor effect for reducing of melt viscosity of the toner, and consequently the toner images are easily peeled off by sliding friction with the magnetic head because of having reduced fixing strength. Furthermore, the toner images are easily stripped off when they are brought in contact with other articles or when a tape is allowed to adhesion thereto.

The term "DSC melting point" used in this specification means an endothermic peak temperature, which can be measured by means of a measuring device: SSC-5200 made by Seiko Instruments Inc. by a method which comprises increasing the

temperature from 20°C to 150°C at a rate of 10°C /minute and then cooling rapidly from 150°C to 20°C, repeating this step twice and measuring the endothermic peak temperature of the second step.

Examples of the wax include polyolefin wax such as polypropylene having a low molecular weight, paraffin wax, Fischer-Tropsch wax, carnauba wax, candelilla wax, rice wax, etc. These waxes can be used alone or as a mixture of them. Of these waxes, Fischer-Tropsch waxes of natural gas type or coal type are preferred to use. The above-mentioned Fischer-Tropsch wax has excellent low temperature fixability as compared with olefin wax, because of having a lower melting point than the olefin wax. It also has excellent preservation stability as compared with conventional petroleum or coal type paraffin wax, because of having a very small amount of low melting point component.

The Fischer-Tropsch wax of natural gas type is particularly preferred to use in the present invention. It is because the Fischer-Tropsch wax of natural gas type gives excellent anti-offsetting property against a thermal fixing roll and excellent preservation stability to the toner. Further, it can be produced in low cost, because the production is free from a step of taking a blue water gas in the case of coal type.

The above-mentioned two types of the Fischer-Tropsch wax are preferred to have a penetration number of 2 or less at 25°C measured by JIS K-2235. If it is larger than 2, the toner has poor fluidity and easily causes trouble in preservation stability and triboelectric charging property.

The content of the wax in the toner is preferred in a range of 2.0 - 15% by weight, and preferably 4.0 - 10% by weight. When the content of wax is lower than 2.0% by weight, it exhibits an inferior effect as the releasing agent and causes problem

in anti-offsetting property and resistance against sliding friction. The content of more than 15% by weight causes trouble in preservation stability.

[0011]

The toner according to the present invention is preferred to contain a charge controlling agent. Specific examples of the positive charge controlling agent include nigrosine and modified material thereof with metal salt of fatty acid, quaternary ammonium salts such as tributylbenzylammonium-1-hydroxy-4-naphthosulfonate, tetrabutylammonium tetrafluoroborate, etc., di-organo-tin oxides such as dibutyltin oxide, dioctyltin oxide, dicyclohexyltin oxide, etc., di-organo-tin borates such as dibutyltin borate, dioctyltin borate, dicyclohexyltin borate, etc., which can be used alone or as a combination of two or more thereof. Of these, nigrosine compounds and quaternary ammonium salts are particularly preferred to use. A preferable amount to be added of them is in a range of 0.1 - 5% by weight.

Specific examples of the negative charge controlling agent include organometallic compounds and chelate compounds such as acetylacetone metal chelate, monoazo metallic chelate, metallic chelate or salt of naphthoic acid or salicylic acid, which can be used alone or as a combination of two or more thereof. Of these, salicylic acid type metal chelate and monoazo metal chelate are particularly preferred to use. A preferable amount to be added of them is in a range of 0.1 - 5% by weight. In the toner of the present invention, though the negative charge controlling agent is preferred to use, the charging property can be controlled by using suitably the above mentioned both charge controlling agents.

[0012]

Since the toner for MICR of the present invention contains

black magnetite particles, no coloring agent may be used commonly. However, the coloring agent can be used, if necessary. Specific examples of the coloring agent include carbon black, aniline blue, charcoil blue, chrome yellow, ultramarine blue, quinoline yellow, methylene blue chloride, phthalocyanine blue, Malachite Green oxalate, lamp black, rose bengale, rhodamine dyes, anthraquinone dyes, monoazo and disazo pigments, mixtures of them, etc. The coloring agent should be incorporated in such an amount that toner images having sufficient image density are formed, and it is generally preferred to be added in an amount of 20 parts by weight based on 100 parts by weight of the binder resin.

[0013]

Further, higher fatty acid, olefin-maleic acid anhydride copolymer, etc. may be suitably added to the toner of the present invention in order to protect the photosensitive member and to obtain toner images having high quality without deterioration of developing property.

Moreover, in the toner of the present invention, it is preferred to attach a fluidizing agent to the surface of toner particles. Typical examples of the fluidizing agent include silica and titanium dioxide, and hydrophobic silica is preferred.

The present invention can be applied to toners for producing by not only a method of melting with kneading the mixture and pulverizing the resultant mass but also a method of polymerizing monomers.

Furthermore, the toner of the present invention can be used not only for the MICR printers but also for common printers.

[0014]

[EXAMPLE]

The present invention will be illustrated in the

following with reference to examples and comparative examples. The present invention however is not restricted to these examples. All parts used hereinbelow are based on weight.

<Example 1>

Styrene-acrylic acid ester copolymer resin 54.0 parts
(Trade name: CPR-100, manufactured by Mitsui Chemicals, Inc.)

Negative charge controlling material 1.5 parts
(Trade name: TRH, manufactured by Hodogaya Chemical Co., Ltd.)

Granular magnetite 30.0 parts
(Trade name: BL-100, manufactured by Titan Kogyo K.K., residual magnetization: 8.5 emu/g, saturation magnetization: 85 emu/g)

Acicular magnetite 12.0 parts
(Trade name: MAT-230, manufactured by Toda Kogyo Corp.; residual magnetization: 30 emu/g, saturation magnetization: 81.8 emu/g)

Natural gas type Fischer-Tropsch wax 2.5 parts
(Trade name: FT-100, manufactured by Nippon Seirou Co., Ltd., melting point: 91°C)

The above-mentioned starting materials were dry-blended by a super mixer and kneaded in a melted state with heat by a twin-screw kneading extruder. The resultant kneaded mixture was then pulverized by a jet mill and classified by an air stream classifier to obtain a toner having a volume average particle diameter of 8 micrometers.

To 100 parts of the above-mentioned toner, 1.5 parts of hydrophobic silica (trade name: R972, manufactured by Nippon Aerosil Co., Ltd.) were added, followed by stirring by a Henschel mixer for 5 minutes so as to adhere to the surface of the toner particles, thereby a toner for MICR of the present invention being obtained.

<Example 2>

Polyester resin 54.0 parts
(Trade name: FC-1198, produced by Mitsubishi Rayon Co., Ltd.)

Negative charge controlling material 1.5 parts
(Trade name: Bontron S-44, manufactured by Orient Chemical Industries, Ltd.)

Granular magnetite 30.0 parts
(Trade name: BL-200, manufactured by Titan Kogyo K.K.; residual magnetization: 8.5 emu/g, saturation magnetization: 85 emu/g)

Acicular magnetite 12.0 parts
(Trade name: CJ-3000B, manufactured by Kanto Denka Kogyo Co., Ltd.; residual magnetization: 34.3 emu/g, saturation magnetization: 83.2 emu/g)

Natural gas type Fischer-Tropsch wax 2.5 parts
(Trade name: FT-100, manufactured by Nippon Seiro Co., Ltd.; melting point: 91°C)

The above-mentioned starting materials were dry-blended by a super mixer and kneaded in a melted state with heat by a twin-screw kneading extruder. The resultant kneaded mixture was then pulverized by a jet mill and classified by an air stream classifier to obtain a negatively charging toner having a volume average particle diameter of 8 micrometers.

To 100 parts of the above-mentioned toner, 2.5 parts of hydrophobic silica (trade name: R972, manufactured by Nippon Aerosil Co., Ltd.) were added, followed by stirring by a Henschel mixer for 5 minutes so as to adhere to the surface of the toner particles, thereby a toner for MICR of the present invention being obtained.

[0015]

<Comparative Example 1>

A toner for comparison was produced by the same manner

as in Example 1 except that 40 parts of granular magnetite: BL-100 and 16 parts of acicular magnetite: MAT-230 were used.

<Comparative Example 2>

A toner for comparison was produced by the same manner as in Example 1 except that 7.5 parts of granular magnetite: BL-100 and 3 parts of acicular magnetite: MAT-230 were used.

<Comparative Example 3>

A toner for comparison was produced by the same manner as in Example 1 except that 27 parts of granular magnetite: BL-100 and 15 parts of acicular magnetite were used.

<Comparative Example 4>

A toner for comparison was produced by the same manner as in Example 1 except that 42 parts of granular magnetite: BL-100 were used alone instead of the magnetite in Example 1.

<Comparative Example 5>

A toner for comparison was produced by the same manner as in Example 1 except that 42 parts of acicular magnetite: MAT-100 were used alone instead of the magnetite in Example 1.

<Comparative Example 6>

A toner for comparison was produced by the same manner as in Example 1 except that polypropylene wax (Viscol 550P, manufactured by Sanyo Chemical Industries, Ltd.; melting point 145℃) was used.

[0016]

<Test for evaluation>

Image density, fog, rub fixing strength, tape peeling strength and signal strength of toner images which were obtained by printing with toners of Examples and Comparative Examples by means of a magnetic single-component type printer (printing rate of A4: 16 sheets/minute) available in the market were evaluated. Results are shown in Table 1.

Table 1

	Image density Initial/ 10,000 sheets	Fog Initial/ 10,000 sheets	Rub fixing strength (survival rate %)	Tape peeling strength (survival rate %)	Signal strength (1) Initial/ 10,000 sheets	Signal strength (2) First time/ 20 times	Signal strength (3) Before peeling/after peeling
Ex.1	1.38/1.38	0.05/0.12	98.1	92.2	163/167	165/162	165/162
Ex.2	1.39/1.37	0.13/0.21	97.8	93.8	170/166	168/166	166/166
Com. Ex.1	1.40/1.39	0.21/0.16	80.3	75.0	215/201	210/161	212/153
Com. Ex.2	1.38/1.37	0.32/0.22	98.8	95.1	59/62	63/61	60/59
Com. Ex.3	1.39/1.38	0.11/0.18	97.6	91.9	212/188	208/175	210/175
Com. Ex.4	1.38/1.37	0.13/0.16	97.9	93.5	67/56	60/55	63/58
Com. Ex.5	1.38/1.39	0.18/0.22	78.9	68.9	321/333	320/200	318/220
Com. Ex.6	1.39/1.37	0.28/0.35	81.2	78.9	165/168	166/102	167/68

In Examples 1 and 2, there was no problem in all of the image density, fog, rub fixing strength, tape peeling strength and signal strength.

In Comparative Example 1, the rub fixing strength and the tape peeling strength were low values and initial signal strength exceeded the appropriate range, because of a large amount of the magnetite.

In Comparative Example 2, the signal strength was below the appropriate range because of a small amount of the magnetite.

In Comparative Example 3, initial signal strength exceeded the appropriate range because of the ratio of acicular magnetite being high.

In Comparative Example 4, the signal strength is below the appropriate range because of using the granular magnetite alone.

In Comparative Example 5, the rub fixing strength and the tape peeling strength were low values and initial signal strength remarkably exceeded the appropriate range because of using the acicular magnetite alone.

In Comparative Example 6, the rub fixing strength and the tape peeling strength were low values and initial signal strength exceeded the appropriate range, because of a large amount of the magnetite.

[0017]

Methods of evaluation are as follows.

1) Image density:

Initial mage density of a solid toner image having a size of 25 mm x 25 mm and image density after printing 10,000 sheets were measured by a reflection densitometer (RD914) manufactured by Aretag Mac Beth LLC.

2) Fog:

Whiteness of non-image areas was measured by a

color-difference meter: ZE2000 made by Nippon Denshoku Industries Co., Ltd., and the initial fog and the fog after printing 10,000 sheets were evaluated as the values of the formula:

(whiteness prior to printing - whiteness after printing).

3) Rub fixing strength (survival rate %):

A solid toner image having a size of 25 mm x 25 mm was rubbed back and forth 3 times by a sand-containing eraser under pressure at 500g/cm^2. The rub fixing strength was calculated from image density X before rubbing and image density Y after rubbing according to the following formula. The resulted value was used in place of the strength against sliding friction with the magnetic head.

Rub fixing strength (%)=Y/X x 100

4) Tape peeling strength (survival rate %):

A cellophane tape was allowed to adhere to a solid toner image having a size of 25 mm x 25 mm and then peeled it off. The tape peeling strength was calculated from image density P before peeling and image density Q after peeling according to the following formula. The resulted value was used in place of the fixing strength of the image in case of contacting with other articles or when tapes were adhered.

Tape peeling strength (%)=Q/P x 100

5) Signal strength (%):

Signal strength was measured by MINI MICR RS232 manufactured by Magtek Co. as an MICR character reader. When the signal strength is in a range of 70 - 200%, it is evaluated that no reading error is caused in the reader sorter of the MICR system reader.

5-1) Signal strength (1):

Initial signal strength and signal strength after reading 10,000 sheets were measured.

5-2) Signal strength (2):

Signal strength of the toner image on one sheet was measured twenty times repeatedly. The value of the first time and the value of 20th time were recorded as the signal strength.

5-3) Signal strength (3):

A cellophane tape was allowed to adhere on MICR characters and then peeled off. Signal strength before peeling and signal strength after peeling were then measured.

[0018]

[EFFECT OF THE INVENTION]

Since the toner for MICR according to the present invention contains granular magnetite and acicular magnetite in a specific ratio and a wax having a specific melting point measured by DSC, it has good MICR ability that appropriate magnetization for reading by the magnetic head is obtained and that the MICR characters are not peeled off by repeated sliding friction with the magnetic head, by which the magnetic head or around MICR characters are not stained to cause no reading error by the reader sorter of the reading machine, and also has good printability that it can be used in the conventional printer for one-component magnetic toner without causing trouble in image qualities such as image density, fog, etc. Therefore, it becomes possible to easily prepare MICR documents (bills and checks) by a one-component magnetic developing system.

[DOCUMENT] ABSTRACT

[ABSTRACT]

[Object] The present invention is to provide a toner for MICR having sufficient resistance against sliding friction with the magnetic head, having appropriate signal strength by which reading errors are not caused, and having no trouble in image qualities such as image density, fog, etc.

[MEANS FOR SOLUTION]

A toner for MICR of the invention comprises a binder resin, magnetite particles and a wax, said magnetite particles comprising granular magnetite and acicular magnetite, wherein a ratio by weight of said acicular magnetite in said magnetite particles is 0.1 - 0.5 to the granular magnetite of 1.0, said magnetite particles are included in an amount of 15 - 50 % by weight in the toner, and said wax has a melting point measured by DSC of 60 - 100°C.

It is preferred that said granular magnetite has residual magnetization of 5 -15 emu/g and saturation magnetization of 70 - 95 emu/g, and said acicular magnetite has residual magnetization of 20 - 50 emu/g and saturation magnetization of 70 - 95 emu/g.

A natural gas type Fischer-Tropsch wax is preferred to use as the Fischer-Tropsch wax.

[ELECTED DRAWING] None

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[Name] Tomoegawa Paper Co., Ltd.

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[List of submitting Material]

[Material] Specification 1

[Material] Abstract 1

[Proof] Require

[DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] TONER FOR MICR

[Claim 1] A toner for MICR which comprises a binder resin, magnetite particles comprising a mixture of granular magnetite and acicular magnetite, and charge controlling agents, wherein said magnetite particles are included in an amount of 15 - 50 % by weight in the toner, and said charge controlling agent consists of at least two charge controlling materials, at least one of which is a chrome azo dye.

[Claim 2] A toner for MICR according to Claim 1, wherein a ratio by weight of said acicular magnetite in said magnetite particles is 0.10- 0.50 to the granular magnetite of 1.0.

[Claim 3] A toner for MICR according to Claim 1, wherein said granular magnetite has residual magnetization of 5 - 15 emu/g and saturation magnetization of 70 -95 emu/g, and said acicular magnetite has residual magnetization of 20 - 50 emu/g and saturation magnetization of 70 -95 emu/g.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[TECHNICAL FIELD OF THE INVENTION]

The present invention relates to a toner for MICR (magnetic ink character recognition) capable of printing magnetic images by a printer of one-component magnetic developing system.

[0002]

[PRIOR ART]

In recent years, documents capable of magnetic ink character recognition (MICR) and particularly checks or bills have been easily prepared by one-component magnetic

developing system with a magnetic toner. The MICR that is a system of reading magnetized images by a magnetic head is not conveniently used because images are obtained by offset printing with magnetic ink. A process of printing with a two-component developer which has been put to practical use is not also conveniently used, because the process requires a large-sized machine as compared with that for the one-component developer. As small-sized printers, there are those for heat-sensitive transfer processes. However, almost all of them are single-purpose machines for printing only MICR characters. It is accordingly desired to develop a small-sized printer capable of printing characters or symbols together with the MICR characters. Regarding the use for MICR, the one-component developing process has been developed hitherto because of using a compact machine, keeping easy maintenance and being capable of printing images other than MICR characters.

[0003]

In the prior art, magnetic materials having large magnetization were attempted to use for the toner for MICR. Japanese Laid-open Patent Publication Nos. Hei 6-282100 and Hei 7-271085 discloses the use of acicular magnetite. The acicular magnetite has, however, problems that it is easily exposed on the surface of toner particles and is easily released from the toner particles by sliding friction with a magnetic head. Although appropriate saturation magnetization is necessary for development by the one-component magnetic developing process, signal strength becomes too high when the acicular magnetite is added in an amount necessary to development. The amount of the acicular magnetite is restricted because of its

inferior dispersing ability. It is therefore difficult to satisfy both of the saturation magnetization required for development and the residual magnetization required for signal strength. It is furthermore impossible to satisfy every requirement even if it is used together with magnetite of other types.

[0004]

The signal strength is influenced by a deposition amount of the toner, and the deposition amount of the toner is influenced by charging property of the toner. It is therefore very important for the toner for MICR to maintain the stabilized charging property. In order to control the charging property, charge controlling agents are generally used. Selection of the charge controlling agent, however, is not easy to carry out, because the charging property is also influenced by the magnetic material.

[0005]

The Japanese Laid-open Patent Publication Nos. Hei 6-282100, 6-43689 and 7-271085 discloses addition of various kinds of waxes to a toner for MICR in order to improve resistance against sliding friction. The resultant toner however often causes problems in magnetic reading even if the image formed has no problem in reading by eyes.

[0006]

In the prior arts, as above-mentioned, there is no MICR toner which satisfies excellent resistance against sliding friction with the magnetic head and appropriate signal strength without hurting image density and image quality such as, fog, etc.

[0007]

[PROBLEM TO BE SOLVED BY THE INVENTION]

An object of the present invention is accordingly to provide a toner for MICR having stabilized charging property, which keeps appropriate toner images capable of reading by the magnetic head, having sufficient resistance against sliding friction with the magnetic head, by which reading errors are not caused, and having no trouble in image qualities such as image density, fog, etc.

[0008]

[MEANS FOR SOLVING THE PROBLEMS]

A toner for MICR of the present invention comprises a binder resin, magnetite particles comprising a mixture of granular magnetite and acicular magnetite, and charge controlling agents, wherein said magnetite particles are included in an amount of 15 - 50 % by weight in the toner, and said charge controlling agent consists of at least two charge controlling materials, at least one of which is a chrome azo dye.

[0009]

[EMBODIMENTS OF THE INVENTION]

The toner for MICR according to the present invention comprises a binder resin, a magnetic material and a charge controlling agent, as main components. The toner may contain, if necessary, a coloring agent, a releasing agent and other additives. A fluidizing agent may also be allowed to attach to the surface of toner particles.

Specific examples of the binder resin of the toner according to the present invention include homopolymers and copolymers of styrene and substituted styrene such as polystyrene, poly-p-chlorostyrene, polyvinyltoluene, styrene-p- chlorostyrene copolymer, styrene-vinyltoluene

copolymer, etc.; copolymers of styrene and acrylic acid ester such as styrene-methyl acrylate copolymer, styrene-ethyl acrylate copolymer, styrene-n-butyl acrylate copolymer, etc.; copolymers of styrene and methacrylic acid ester such as styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-n-butyl methacrylate copolymer, etc.; styrene-acrylic acid ester-methacrylic acid ester terpolymer; styrene copolymers composed of styrene and other vinyl monomers such as styrene-acrylonitrile copolymer, styrene-vinyl methyl ether copolymer, styrene-butadiene copolymer, styrene-vinyl methyl ketone copolymer, styrene-acrylonitrile-indene copolymer, styrene-maleic acid ester copolymer, etc.; polymethyl methacrylate, polybutyl methacrylate, polyacrylic acid ester resin, polyester resin, polyvinyl acetate, polyamide resin, epoxy resin, polyvinyl butyral resin, polyacrylic acid- phenol resin, phenol resin, aliphatic or alicyclic hydrocarbon resin, petroleum resin, chlorinated paraffin, polyvinyl chloride, polyvinylidene chloride, etc., which can be used alone or as a mixture of two or more of them.

Of these resins, styrene-acrylic acid ester copolymer resin and polyester resin are preferably used in the present invention.

[0010]

The content of the magnetite particles incorporated in the toner for MICR of the present invention should be in a range of 15 - 50% by weight and preferably 20 - 45% by weight. When the amount of the magnetite particles is lower than 15% weight, saturation magnetization necessary for the development and residual magnetization necessary for the development cannot be obtained. When the amount

of it is in excess of 50% by weight, there are problems that fixing strength reduces to cause deterioration of the resistance against sliding friction, that the saturation magnetization is in excess of the value required for the development, and that the signal strength exceeds the appropriate level.

The magnetite particles are composed at least of granular magnetite and acicular magnetite. The ratio by weight of said acicular magnetite in said magnetite particles should be in a range of 0.10 -0.50 to 1.0 of the granular magnetite. A range of 0.20 -0.45, to 1.0 of the granular magnetite is more preferable. When the ratio by weight of the acicular magnetite to the granular magnetite is in excess of 0.5, the signal strength exceeds an appropriate range. On the other, when it is lower than 0.1, the signal strength is lower than the appropriate range due to the lack of desired residual magnetization. As a result, a reader sorter of the MICR reading machine causes reading errors.

The granular magnetite used in the present invention is preferred to have the residual magnetization in a range of 5 - 15 emu/g, and particularly 8 - 13 emu/g. The saturation magnetization of it is preferred to be in a range of 70 - 95 emu/g, and particularly 75 - 85 emu/g. The residual magnetization of lower than 5 emu/g produces a tonner having low residual magnetization to cause lack of the signal strength, while the residual magnetization of higher than 15 emu/g brings about excess magnetization and excess signal strength, to result in reading errors in both cases. When the saturation magnetization is lower than 70 emu/g, such saturation magnetization is insufficient for the development. On the other hand, when

it exceeds 95 emu/g, it shows a tendency to exceeding the saturation magnetization necessary for the development. Conventional granular magnetite having a particle size of 0.2 - 0.3 micrometers and an aspect ratio of less than 2.0 can be used in the present invention.

The granular magnetite used in the present invention include those having irregular, spherical, hexahedral and octahedral shapes.

The acicular magnetite used in the present invention is preferred to have the residual magnetization in a range of 20 - 50 emu/g, and particularly 25 - 40 emu/g. The saturation magnetization of it is preferred to be in a range of 70 - 95 emu/g, and particularly 75 - 85 emu/g. The residual magnetization of lower than 20 emu/g causes the lack of signal strength and that of higher than 50 emu/g brings about excess signal strength. The saturation magnetization of lower than 70 emu/g does not bring the saturation magnetization necessary for the development and that of higher than 95 emu/g shows a tendency to exceeding the saturation magnetization necessary for the development. Conventional acicular magnetite having a particle size of approximately 0.6 micrometers and an aspect ratio of 2.0 or more can be used in the present invention.

[0011]

The toner for MICR according to the present invention is necessary to contain at least 2 kinds of charge controlling materials, at least one of which is a chrome azo dye. Namely, as shown in Examples 1 and 2 and Comparative Examples 6, 7 and 8, it is necessary to satisfy the following two requirements. (1) Two or more charge controlling materials are contained in the toner, and (2) one or more chrome azo dyes are contained in the

toner as the charge controlling agent.

The charge controlling agent is influenced by change of environmental conditions or continuous printing of numbers of sheets to cause change of an charging amount of the toner or change of amount of the developed toner, thereby resulting in a change of image density and fogging. In such a case, even if the image density has no problem in practical use for conventional documents, it causes problems when it is used for MICR, because the signal strength often departs from the appropriate range by a slight change of the amount of the developed toner to cause reading errors in the reader sorter of the MICR reading machine. Accordingly, selection of the charge controlling agent should be carried out very strictly as compared with the conventional toner for copying. The present inventor has completed the present invention as a result of earnest studies concerning the charge controlling agent.

By the way, Examples 1 and 2 satisfy the above-mentioned two requirements, but Comparative Example 6 does not satisfy the requirement (1), Comparative Example 7 does not satisfy the requirement (2), and Comparative Example 8 does not satisfy the requirements (1) and (2). Therefore, the image density after copying 20000 sheets varies so that the signal strength departs from the appropriate range.

The charge controlling agent is classified into a charge controlling material which affords positive charge to the toner and a charge controlling material which affords negative charge to the toner. Specific examples of the positive charge controlling material include nigrosine and modified material thereof with metal salt of

fatty acid, quaternary ammonium salts such as tributylbenzylammonium-1-hydroxy-4-naphthosulfonate, tetrabutylammonium tetrafluoroborate, etc., di-organo-tin oxides such as dibutyltin oxide, dioctyltin oxide, dicyclohexyltin oxide, etc., di-organo-tin borates such as dibutyltin borate, dioctyltin borate, dicyclohexyltin borate, etc., which can be used alone or as a combination of two or more thereof. Of these, nigrosine compounds and quaternary ammonium salts are particularly preferred to use.

Specific examples of the negative charge controlling material include organometallic compounds and chelate compounds such as acetylacetone metal chelate, monoazo metallic chelate, metallic chelate or salt of naphthoic acid or salicylic acid, which can be used alone or as a combination of two or more thereof. Of these, salicylic acid type metal chelate and monoazo metal chelate are particularly preferred to use. The chrome azo dye required in the present invention belongs to metal chelate monozao dye.

A preferable amount to be added of the charge controlling agent is in a range of 0.1 - 10% by weight, and preferably 1.0 - 5.0 % by weight to the toner.

[0012]

It is preferred that the toner of the present invention contains a releasing agent in order to ensure excellent releasing property of a heating roll for fixation or to ensure the excellent resistance against sliding friction with the magnetic head.

Examples of the releasing agent include waxes, higher fatty acids, higher fatty acid amides, hydrogenated castor oil, etc. Specific examples of the wax include

polyolefin wax such as polyethylene and polypropylene having a low molecular weight, paraffin wax, Fischer-Tropsch wax, carnauba wax, candelilla wax, rice wax, etc. These waxes can be used alone or as a mixture of them.

In the present invention, polyolefin wax is preferred to use as the releasing agent because of having excellent anti-offsetting property. It is because the offset sometimes causes reading error in MICR even though the printed image has no visual problem.

The content of the releasing agent is preferred in a range of 1.5 - 15% by weight, and preferably 2 - 10% by weight in the toner.

[0013]

Since the toner for MICR of the present invention contains black magnetite particles, no coloring agent may be used commonly. However, the coloring agent can be used, if necessary. Specific examples of the coloring agent include carbon black, aniline blue, charcoil blue, chrome yellow, ultramarine blue, quinoline yellow, methylene blue chloride, phthalocyanine blue, Malachite Green oxalate, lamp black, rose bengale, rhodamine dyes, anthraquinone dyes, monoazo and disazo pigments, mixtures of them, etc. The coloring agent should be incorporated in such an amount that toner images having sufficient image density are formed, and it is generally preferred to be added in an amount of 20 parts by weight based on 100 parts by weight of the binder resin.

[0014]

Further, higher fatty acid, olefin-maleic acid anhydride copolymer, etc. may be suitably added to the toner of the present invention in order to protect the photosensitive member and to obtain toner images having

high quality without deterioration of developing property.

Moreover, in the toner of the present invention, it is preferred to attach a fluidizing agent to the surface of toner particles. Typical examples of the fluidizing agent include silica and titanium dioxide, and hydrophobic silica is preferred.

The present invention can be applied to toners for producing by not only a method which comprises melting with kneading the mixture and pulverizing the resultant mass but also a method of polymerizing monomers.

Furthermore, the toner of the present invention can be used not only for the MICR printers but also for common printers.

[0015]

[EXAMPLES]

The present invention will be illustrated in the following with reference to examples and comparative examples. The present invention however is not restricted to these examples. All parts used hereinbelow are based on weight.

<Example 1>

Styrene-acrylic acid ester copolymer resin 56.0 parts
(Trade name: CPR-100, manufactured by Mitsui Chemicals, Inc.)

Negative charge controlling material 0.5 parts
Calix[n]arene compound
(Trade name: E-89, manufactured by Orient Chemical Ind., Ltd.)

Negative charge controlling material 1.0 parts
(Chrome azo dye; Trade name: TRH, manufactured by Hodogaya Chemical Co., Ltd.)

Granular magnetite 28.0 parts

(Trade name: BL-100, manufactured by Titan Kogyo K.K.;
residual magnetization: 8.5 emu/g,
saturation magnetization: 85 emu/g)

Acicular magnetite 12.0 parts
(Trade name: MAT-230, manufactured by Toda Kogyo Corp.;
residual magnetization: 30 emu/g,
saturation magnetization: 81.8 emu/g)

Polypropylene wax 2.5 parts
(Trade name: Viscol 550P, manufactured by Sanyo Chemical Industries, Ltd.)

The above-mentioned starting materials were dry-blended by a super mixer and kneaded in a melted state with heat by a twin-screw kneading extruder. The resultant kneaded mixture was then pulverized by a jet mill and classified by an air stream classifier to obtain a toner having a volume average particle diameter of 8 micrometers.

To 100 parts of the above-mentioned toner, 1.5 parts of hydrophobic silica (trade name: R972, manufactured by Nippon Aerosil Co., Ltd.) were added, followed by stirring by a Henschel mixer for 5 minutes so as to attach to the surface of the toner particles, thereby a toner for MICR of the present invention being obtained.

<Example 2>

Polyester resin 55.5 parts
(Trade name: FC-1198, manufactured by Mitsubishi Rayon Co., Ltd.)

Negative charge controlling material 1.0 parts
(Chrome azo dye; Trade name: TRH, manufactured by Hodogaya Chemical Co., Ltd.)

Negative charge controlling material 1.0 parts
(Chrome azo dye; Trade name: Bontron S-34, manufactured

by Orient Chemical Ind., Ltd.)

Granular magnetite 28.0 parts

(Trade name: EPT-500, manufactured by Titan Kogyo K.K.; residual magnetization: 11.6 emu/g, saturation magnetization: 83.0 emu/g)

Acicular magnetite 12.0 parts

(Trade name: CJ-3000B, manufactured by Kanto Denka Kogyo Co., Ltd.; residual magnetization: 34.3 emu/g, saturation magnetization: 83.2 emu/g)

Polyethylene wax 2.5 parts

(Trade name: PE-130, manufactured by Hoechst A.G.)

The above-mentioned starting materials were dry-blended by a super mixer and kneaded in a melted state with heat by a twin-screw kneading extruder. The resultant kneaded mixture was then pulverized by a jet mill and classified by an air stream classifier to obtain a negatively charging toner having a volume average particle diameter of 8 micrometers.

To 100 parts of the above-mentioned toner, 2.5 parts of hydrophobic silica (trade name: R972, manufactured by Nippon Aerosil Co., Ltd.) were added, followed by stirring by a Henschel mixer for 5 minutes so as to attach to the surface of the toner particles, thereby a toner for MICR of the present invention being obtained.

[0016]

<Comparative Example 1>

A toner for comparison was produced by the same manner as in Example 1 except that 37 parts of granular magnetite: BL-100 and 15 parts of acicular magnetite: MAT-230 were used and the amount of the binder resin was changed to 44 parts.

<Comparative Example 2>

A toner for comparison was produced by the same manner as in Example 1 except that 35 parts of granular magnetite: BL-100 and 17 parts of acicular magnetite: MAT-230 were used and the amount of the binder resin was changed to 44 parts.

<Comparative Example 3>

A toner for comparison was produced by the same manner as in Example 1 except that 7.5 parts of granular magnetite: BL-100 and 3.0 parts of acicular magnetite: MAT-230 were used and the amount of the binder resin was changed to 85.5 parts.

<Comparative Example 4>

A toner for comparison was produced by the same manner as in Example 1 except that 40 parts of granular magnetite: BL-100 were used alone instead of the magnetite in Example 1.

<Comparative Example 5>

A toner for comparison was produced by the same manner as in Example 1 except that 40 parts of acicular magnetite: MAT-230 were used alone instead of the magnetite in Example 1.

<Comparative Example 6>

A toner for comparison was produced by the same manner as in Example 1 except that only the chrome azo dye: TRH was used in an amount of 1.5 parts as the charge controlling material.

<Comparative Example 7>

A toner for comparison which did not contain chrome azo dye was produced by the same manner as in Example 1 except that the chrome azo dye: TRH was replaced with LR147(boron contaianing organic material, manufactured by Nippon Carlit Co.).

<Comparative Example 8>

A toner for comparison was produced by the same manner as in Example 1 except that only E-89 was used in an amount of 1.5 parts as the charge controlling agent and the chrome azo dye was not used.

[0017]

<Test for evaluation>

Image density, fog, rub fixing strength, tape peeling strength and signal strength of the toner images which were obtained by printing with toners of Examples and Comparative Examples by means of a magnetic single-component type printer (printing rate of A4: 16 sheets/minute) available in Table 1 the market were evaluated. Results are shown in.

Methods of evaluation are as follows.

1) Image density:

Initial mage density of a solid toner image having a size of 25 mm x 25 mm and image density after printing 20,000 sheets were measured by a reflection densitometer (RD914) manufactured by Aretag Mac Beth LLC.

2) Fog:

Whiteness of non-image areas were measured by a color-difference meter: ZE2000 manufactured by Nippon Denshoku Industries, Co., Ltd., and the initial fog and the fog after copying 20,000 sheets were evaluated as the value of the formula:

(whiteness prior to printing - whiteness after printing).

3) Rub fixing strength (survival rate %):

A solid toner image having a size of 25 mm x 25 mm was rubbed back and forth 3 times by a sand-containing eraser under pressure at 500g/cm^2. The rub fixing strength

was calculated from image density X before rubbing and image density Y after rubbing according to the following formula. The resulted value was used in place of the strength against sliding friction with the magnetic head.

Rub fixing strength (%)=Y/X x 100

4) Tape peeling strength (survival rate %):

A cellophane tape was allowed to adhere to a solid toner image having a size of 25 mm x 25 mm and then peeled it off. The tape peeling strength was calculated from image density P before peeling and image density Q after peeling according to the following formula. The resulted value was used in place of the fixing strength of the image in case of contacting with other articles or when tapes were adhered.

Tape peeling strength(%)=Q/P x 100

5) Signal strength (%):

Initial signal strength and signal strength after printing 20,000 sheets were measured by MINI MICR RS232 made by Magtek Co. as an MICR character reader. When the signal strength is in a range of 70 - 200%, it is evaluated that no reading error is caused in the reader sorter of the MICR system reader.

Table 1

	Image density Initial/ 20,000 sheets	Fog Initial/ 20,000 sheets	Rub fixing strength (survival rate %)	Tape peeling strength (survival rate %)	Signal strength (%) Initial/ 20,000 sheets
Ex.1	1.38/1.39	0.27/0.31	98.3	93.3	165/171
Ex.2	1.40/1.39	0.26/0.33	98.0	94.1	169/176
Com. Ex.1	1.42/1.45	0.62/0.28	81.8	78.0	206/221
Com. Ex.2	1.43/1.44	0.39/0.46	78.0	73.2	221/233
Com. Ex.3	1.37/1.37	0.44/0.46	98.8	94.5	63/64
Com. Ex.4	1.38/1.40	0.45/0.69	98.5	93.8	75/66

Com. Ex.5	1.37/1.38	0.22/0.79	78.5	69.0	341/356
Com. Ex.6	1.36/1.43	0.41/0.18	98.2	92.8	136/225
Com. Ex.7	1.39/1.22	0.31/0.30	97.5	93.2	142/68
Com. Ex.8	1.38/1.18	0.33/0.48	97.2	92.2	140/53

As be shown in Table 1, the toners for MICR according to Examples 1 and 2 were confirmed to have satisfactory properties for practical MICR in the image density, fog, rub fixing strength, tape peeling strength and signal strength throughout continuous printing of 20,000 sheets.

In Comparative Example 1 and 2, fixing strength is inferior and the signal strength exceeded 200% that was the upper limit of the appropriate range throughout continuous printing of 20,000 sheets, because of a large amount of the magnetite.

In Comparative Example 3, the signal strength was lower than 70% which was the lower limit of the appropriate range throughout continuous printing of 20,000 sheets, because of a small amount of the magnetite.

In Comparative Example 4, the signal strength was lower than 70% that was the lower limit of the appropriate range throughout printing when the printing of 20,000 sheets was carried out continuously, because of using the granular magnetite alone.

In Comparative Example 5, fixing strength is inferior and the signal strength exceeded 200% that was the upper limit of the appropriate range throughout continuous printing of 20,000 sheets, because of using the acicular magnetite alone.

In Comparative Example 6, image density after printing 20,000 sheets increased and the signal strength

exceeded 200% that was the upper limit of the appropriate range, because of using only the chrome azo dye as the charge controlling agent.

In Comparative Example 7, image density after printing 20,000 sheets reduced and the amount of the toner developed became small so that the signal strength was lower than 70% that was the lower limit of the appropriate range, because of using the two kinds of charge controlling materials excluding the chrome azo dye.

In Comparative Example 8, image density after printing 20,000 sheets reduced and the amount of the toner developed became small so that the signal strength was lower than 70% that was the lower limit of the appropriate range, because of using only one charge controlling agent which was not the chrome azo dye.

[0019]

[EFFECT OF THE INVENTION]

The present invention can provide a toner for MICR having stabilized charging property, which keeps appropriate toner images capable of reading by the magnetic head, having sufficient resistance against sliding friction with the magnetic head, by which reading errors are not caused, and having no trouble in image qualities such as image density, fog, etc.

[DOCUMENT] ABSTRACT

[ABSTRACT]

[OBJECT] The object of the invention is to provide a toner for MICR having stabilized charging property, which keeps appropriate toner images capable of reading by the magnetic head, having sufficient resistance against sliding friction with the magnetic head, by which reading errors are not caused, and having no trouble in image qualities such as image density, fog, etc.

[MEANS FOR SOLUTION]

A toner for MICR which comprises a toner for MICR which comprises a binder resin, magnetite particles comprising a mixture of granular magnetite and acicular magnetite, and charge controlling agents, wherein said magnetite particles are included in an amount of 15 - 50 % by weight in the toner, and said charge controlling agent consists of at least two charge controlling materials, at least one of which is a chrome azo dye.

[ELECTED DRAWING] None